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Refractive index studies on heptanol with dimethylktone , ethyl methyl ketone, methyl methacrylate systems at 301K

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ABSTRACT

The refractive index have been measured for the binary mixtures of n-heptanol with dimethylktone , ethyl methyl ketone, methyl methacrylate 301K. The molar refraction, atomic polarization , polarizability and atomic radii and molar volume evaluated. From the refractive index and related parameter study about the nature of interactions.

Keywords: Refractive index, Heptanol , hydroxyl – carbonyl interactions.

INTRODUCTION

Refractive index studies give the valuable knowledge regarding the nature of hydroxyl-carbonyl complexes. [1-3] Lots of workers find out the nature of interactions by the dielectric [4-6], ultrasonic [7-12] infrared [13] measurements. The present investigation, study the nature of the interactions of donor (heptanol) with acceptor (dimethylktone & ethyl methyl ketone) complexes from the refractive index measurements & related refractive index parameter.

MATERIALS AND METHODS

The samples of dimethyl ktone, methyl ethyl ketone , methyl methacrylate and 1-heptanol were used in the present inquiry. Samples were used without further purification. Check the purity of the chemicals by the measurement of refractive index of the pure liquids. Purity is about the samples about 99.99%. The refractive indices of liquid mixtures were measured using Abbes refractometer by using sodium D-Line at 301K. The temperature of the refractometer was maintained at 301K by using water circulated thermostat with constant temperature. The density of the mixture and pure liquids were obtained by the 5ml specific gravity bottles.

As molar refraction is assess of total polarizability of a mole of a substance. It is related to refractive index & temperature. If the changes the molar refraction also changes the refractive index & all other optical parameter. The molar refraction (R) were calculated using the relation Lorentz-Lorentz (LL) equation

$$R = \left[\frac{n^2 - 1}{n^2 + 2}\right]\left[\frac{m_1 x_1 + m_2 x_2}{d_{12}}\right] \quad \ldots(1)$$

The atomic polarization is directly proportional to the square of refractive index. It can be calculated from the equation (2)

Atomic polarization $P_a = 1.05n^2$ …(2)

The dipole moment increases or decreases by the applications electrical field can be calculated from the optical refractive index of a material. The refractive index is related to the polarizability of molecules by Lorentz- Lorentz formula

$$\alpha = \frac{3m}{4\pi N_a d}\left[\frac{n_{12}^2 - 1}{n_{12}^2 + 2}\right] or \frac{3R}{4\pi N_a} \quad \ldots(4)$$

Where N , d, m is the avogadro number , density, molecular weight respectively .

The solvated radii (r_a) have been finding out by assuming the spherical shape of solvated molecules, given by the expression

$$v = \frac{4}{3}\pi r^3 \quad \ldots(5)$$

The molar volume of the pure and binary liquid mixture using the relation (6)

Molar volume of the binary mixture $v_{12} = \frac{m_1 x_1 + m_2 x_2}{d_{12}}$ since $v_1 = \frac{m_1}{d_1}$, $v_2 = \frac{m_2}{d_2}$ …(6)

Here x, m and d designate the mole fraction, the molecular weight and the density of the pure component 1, 2 mixtures 12.

The experimental values were fitted to the equation $x = \sum_j A_j x_1^j$ …(7)

Where, x_1 is the mole fraction of heptanol and b_j is the polynomial coefficients obtained by a linear least-squares fit.

$$\sigma = \frac{\sum \left(y_{mix} - y_{ideal}\right)^2}{\left(m-n\right)^{0.5}} \quad \ldots(7)$$

Where n is the number of experimental data points and m is the number of parameter. The values of coefficients *cj* and the standard deviations *ó* are reported in Table 4.

The refractive index parameter calculated from the equation (1) to (6) and standard deviation from the equation (7). The refractive index parameter reported in table 1 to 3 and the standard deviations reported in table 4.

RESULTS AND DISCUSSION

The experimental values of refractive index & density of the mixtures, over the whole composition range, at 301 K given table 1 to 3 along with the refractive index parameters molar refraction , atomic polarization , atomic polarizability, molecular radii & molar volume evaluated from refractive index measurements. The coefficients & standard deviation are shown in table 4.

Refractive index values of the mixtures altered due to the electronic polarization. Electronic polarization increases than refractive indices increases as shown in table 1 to 3. The refractive indices of the mixtures heptanol with dimethylketone , ethyl methyl ketone & methylmethacrylate increases because of electronic polarization increases. This indicates that may be strong solute solvent interactions taking place in these systems. Similar trend observed in the variation of molar refraction (Fig. 1) & molar volume. Molar refraction related directly to the refractive index. This behavior confirms the existence of solute solvent interactions.

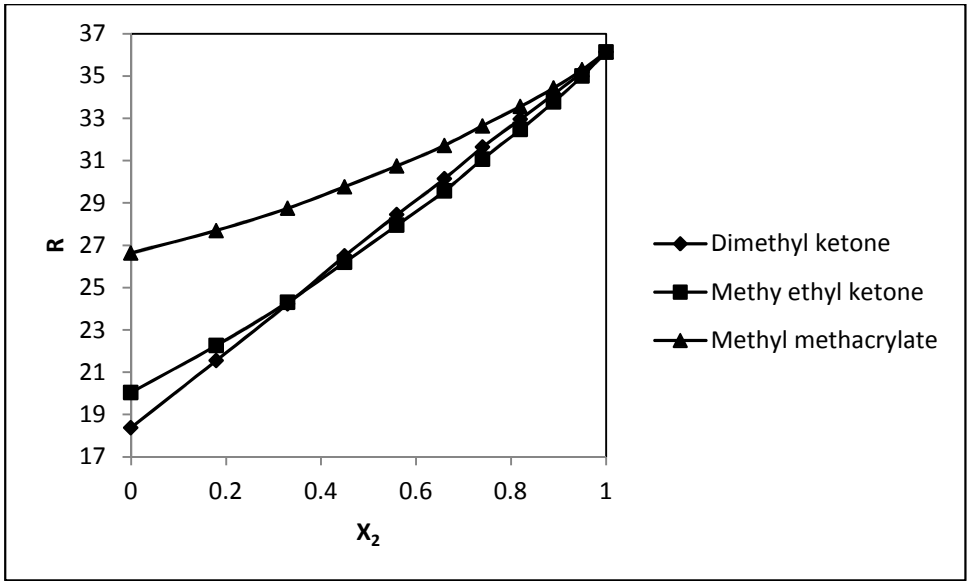

Fig. 1 Plots of molar refraction (R) with the molfraction of heptanol with the carbonyl complexes

The refractive index parameters are not having ideal mixtures behavior. These indicate that existence of 1:1 alcohol – carbonyl complexes. Also discuss about the nature of the solute – solvent interactions.

The molar volume is related to the density of the mixtures. The increasing the concentrations of heptanol molar volume get increased for these mixtures as given in table 1 to 3.. These indicate the atomic packing density decreases simultaneously the donor aceptor atoms are free to interaction taking place.

The density of binary mixtures of heptanol with dimethyl ktone & ethyl methyl ketone increases as shown in table 1 to 3.. The density increases molar volume increases because of the influence of weak solute solvent interactions through polarization, dipole dipole interactions of hydroxyl & carbonyl group.

The density of binary mixtures of heptanol with methyl methacrylate decreases while increasing the concentration of heptanol as given in table 1 to 3.. When decreasing the density of the mixtures molar volume get decreases because of the influence of strong molecular interactions may occurs due to hydrogen.

The atomic polarization is finding from the high permittivity of substance mole of a substance. It is related to refractive index & temperature. If the changes the molar refraction also changes the atomic polarization. The atomic polarization increases with the concentration of hepatnol as shown in table 1 to 3. These indicate the hydrogen bonded 1-heptanol try interaction between the oxygen molecules of carbonyls & hydroxyl group of hydrogen due to the bond broken of heptanol. All the systems, when increasing concentration atomic polarization also increases. These indicate solute solvent interactions exist in these systems.

The values of atomic polarizability increases as the mole fraction increases and also similar trend observed in the molar refraction for all the systems i.e acetone < ethyl methylketone < methyl methacrylate as shown in table 1 to 3. The refractive index and polarizability increases and solute solvent interaction decreases is in the order of dimethyl ktone > ethyl methyl ketone > methyl metahcrylate , 1-heptanol as another liquids.

The values of solvated radii increase with increasing concentration of heptaol for all the systems as showing in table 1 to 3.. This indicate may occur the solute solvent interactions heptanol & carbonyls (dimethylktone , ethyl methyl ketone & methyl methacrylate). The polynomial coefficients & standard deviation explain ideal mixture behavior of these binary systems. The standard deviations of refractive index & density are in the order of methyl methacrylate < dimethylketone < ethyl methyl ketone 1-heptanol as one of the component.

The value of coefficients and standard deviations as given table 4, the standard deviations values indicate the existence of solute solvent interactions of hydroxyl and carbonyl complexes is confirmed.

Table 1: The variation of refractive index (n_{12}), density (d_{12} Kg/m^3), and molar refraction (R), atomic polarization (Pa) , atomic polarizability (α) , solvated radii (r_a) , molar volume (Vcm^3) with the mole fraction (x_2) of 1-heptanol with acetone systems

x_2	n_{12}	d_{12}	R	Pa	α	r_a	V
0	1.414	0.79	18.38	2.1	2.61	5.57	74
0.18	1.416	0.795	21.56	2.105	3.06	5.87	86
0.33	1.417	0.799	24.23	2.109	3.44	6.1	96
0.45	1.418	0.803	26.5	2.112	3.76	6.28	105
0.56	1.419	0.806	28.45	2.115	4.04	6.42	113
0.66	1.42	0.809	30.15	2.117	4.28	6.55	119
0.74	1.421	0.811	31.64	2.119	4.49	6.65	125
0.82	1.421	0.813	32.96	2.121	4.67	6.74	130
0.89	1.422	0.815	34.14	2.123	4.84	6.81	134
0.95	1.423	0.817	35.19	2.125	4.99	6.88	138
1	1.423	0.819	36.14	2.126	5.13	6.94	142

Table 2: The variation of refractive index (n_{12}), density (d_{12} Kg/m^3), and molar refraction (R), atomic polarization (Pa) , atomic polarizability (α) , solvated radii (r_a) , molar volume (Vcm^3) with the mole fraction (x_2) of 1-heptanol with ethyl methyl ketone systems

x_2	n_{12}	d_{12}	R	Pa	α	r_a	V
0	1.358	0.79	20.04	1.936	2.84	5.99	91
0.15	1.368	0.794	22.27	1.964	3.16	6.15	99
0.28	1.377	0.798	24.31	1.99	3.45	6.29	106
0.4	1.384	0.801	26.2	2.012	3.72	6.41	112
0.51	1.392	0.805	27.95	2.033	3.96	6.52	118
0.61	1.398	0.807	29.57	2.052	4.19	6.61	123
0.7	1.404	0.81	31.07	2.069	4.41	6.69	127
0.78	1.409	0.812	32.47	2.085	4.61	6.76	131
0.86	1.414	0.815	33.78	2.1	4.79	6.83	135
0.93	1.419	0.817	35	2.114	4.96	6.89	139
1	1.423	0.819	36.14	2.126	5.13	6.94	142

Table 3: The variation of refractive index (n_{12}), density (d_{12} Kg/m^3), and molar refraction (R), atomic polarization (Pa) , atomic polarizability (α) , solvated radii (r_a) , molar volume (Vcm^3) with the mole fraction (x_2) of 1-heptanol with methyl methacrylate systems

x_2	n_{12}	d_{12}	R	Pa	α	r_a	V
0	1.414	0.94	26.63	2.1	3.78	6.31	107
0.13	1.415	0.924	27.7	2.103	3.93	6.39	111
0.25	1.416	0.91	28.75	2.107	4.08	6.46	114
0.36	1.417	0.896	29.77	2.11	4.22	6.53	118
0.47	1.418	0.883	30.75	2.112	4.36	6.6	122
0.57	1.419	0.871	31.72	2.115	4.5	6.66	126
0.67	1.42	0.859	32.65	2.118	4.63	6.72	129
0.76	1.421	0.848	33.56	2.12	4.76	6.78	132
0.84	1.422	0.838	34.44	2.122	4.89	6.84	136
0.92	1.422	0.828	35.3	2.124	5.01	6.89	139
1	1.423	0.819	36.14	2.126	5.13	6.94	142

Table: 4 The polynomial coefficients and standard deviations (σ) of the refractive index (n) and density (d) of the binary mixtures

Property	A_0	A_1	A_2	A_3	A_4	A_4	σ
Heptanol+dimethyl ktone							
n	1.414	0.013	-0.035	0.008	-0.19	0.24	2.8
d	0.790	0.012	-0.045	0.02	-0.18	0.24	2.4
Heptanol+ ethyl methyl ketone							
n	1.358	0.050	0.08	-0.006	-0.2	0.14	3.2
d	0.792	0.06	0.07	-0.007	-0.1	0.14	3.2
Heptanol+methyl methaacrylate							
n	1.414	0.07	-0.2	-0.032	0.45	0.0009	2.6
d	0.945	0.05	-0.4	-0.04	0.44	0.005	2.1

CONCLUSION

The variation of refractive index & density indicate that may exist in the solute solvent interactions. Refractive index parameter molar refraction, atomic polarization, electronic polarazibility, solvated radii, & molar volume, coefficients of density, refractive index & standard deviations confirmed the solute solvent interactions. The experimental values & refractive index parameter indicate the order of interactions methyl metha acrylate < methyl ethyl ketone < dimethylketone, 1-heptaonol as one of the piece.

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